

**JOURNAL**  
OF THE  
**OIL AND COLOUR CHEMISTS'**  
**ASSOCIATION**



1465

**Plasticisers and Polymers Derived from Fats**

*By* W. C. AULT.

[Vol. 43, No. 9 September, 1960]

OIL & COLOUR CHEMISTS' ASSOCIATION  
WAX CHANDLERS' HALL,  
GRESHAM STREET, LONDON, E.C.2

# Plasticisers and Polymers Derived from Fats\*

By W. C. AULT

*Eastern Utilisation Research and Development Division, Agricultural Research Service,  
U.S. Department of Agriculture, Philadelphia, Pennsylvania, U.S.A.*

## Summary

The extensive use of polymers and plasticisers, coupled with the potential advantages of the long straight-chain structures of the fatty acids in their manufacture, has led to investigation in this field. Early efforts to find fatty derivatives for use as plasticisers were directed toward the hydroxy acids. Of this group methyl diacetoxystearate shows some promise. The compatibility requirement that it be essentially free of methyl stearate and methyl hydroxystearate may be a significant factor in preventing its commercial use.

The manufacture of epoxidised fatty derivatives for use as plasticisers has increased since the discovery of their stabilising effect on p.v.c. compositions. Soyabean oil has usually been chosen for epoxidation because it is cheap and plentiful, but the product cannot be used as a primary plasticiser because its compatibility is limited. Research in this area has led to primary solvent type plasticisers of the epoxy type, such as the alkyl epoxystearates and epoxidised acetoglycerides.

A novel class of fatty derivatives having potential value as plasticisers are those with a phosphorus to carbon bond. The 9, 10-trialkyl phosphonostearates are noteworthy, having a low migration loss and generally imparting good low temperature characteristics to p.v.c.

The preparation of vinyl stearate and of its homo- and co-polymers has been studied and commercial production has resulted. Other types of fatty materials investigated include the long chain alkyl acrylates and vinyl epoxystearate. New types of polymers have been prepared by the condensation of epoxidised oils with phthalic anhydride in the presence of certain organic bases.

## INTRODUCTION

The annual production of inedible animal fats in the United States is currently about 3 billion pounds or 1.5 million tons. During the past dozen years the production rate has increased substantially while the principal outlet in the soap kettle has diminished by half. Research aimed at increasing the industrial outlets appears to be one of the most promising avenues for increasing our domestic fat consumption. Such research inevitably will be directed toward the large scale industrial outlets for organic materials among which plasticisers and polymers occupy an important place.

---

\*Paper presented before the London Section of the Oil & Colour Chemists' Association and the Oils and Fats Group of the Society of Chemical Industry, London, 22 October, 1959.

## PLASTICISERS

*Hydroxystearic Acids and Their Derivatives*

Fats and numerous compounds simply or directly derived from them have most of the characteristics desired in a plasticiser. For the most part they are inexpensive. Moreover, they have low vapour pressures, good water resistance, freedom from objectionable odour and colour, and good stability. Their commercial use as plasticisers has been slow to develop, however, because except for the dibasic acid derivatives, compatibility with commercial plastics is lacking.

Our first efforts to find commercially feasible fat derivatives for use as plasticisers were directed toward investigation of the compatibility of some relatively simple derivatives of 9, 10-dihydroxystearic acid and 9, 10-dihydroxyoctadecanol with some commercial polymers<sup>1</sup>. Generally poor compatibility characteristics indicated considerable limitations upon the use of these materials.

More recently a number of acyloxy and aryloxy esters prepared from hydroxystearic acids have been evaluated as plasticisers for a 95 : 5 vinyl chloride-vinyl acetate copolymer<sup>2</sup>. Several of them were found to be primary plasticisers, having very good low-temperature performance when employed at the 35 per cent level. Of this group, butyl diacetoxystearate showed overall characteristics having considerable promise. The compatibility requirement that it be essentially free of butyl stearate and butyl hydroxystearate may be a significant factor in preventing its commercial use.

*Epoxidised Fats and Fat Derivatives*

Some time ago workers in this laboratory reported a convenient and practical method for the epoxidation of unsaturated fatty materials with organic peracids<sup>3</sup>. It was also noted that the compatibility of these long chain compounds with a variety of resins was improved by the introduction of the oxirane group and the use of the epoxidised materials as plasticisers was suggested<sup>1</sup>. Substantial industrial use for this class of materials developed following the observation that they are excellent light and thermal stabilisers for polyvinyl chloride when used to the extent of 1 to 5 per cent of the formulation. This effect of the epoxidised fats is particularly notable when they are used in combination with certain metal salts and chelating compositions.

Industrially soyabean oil has been preferred for epoxidation because it is cheap and plentiful, it can be epoxidised to a relatively high oxirane content (5.8 to 7.0 per cent), and its volatility loss from polyvinyl chloride is low. Epoxidised soyabean oil cannot be used as a primary plasticiser, however, because its compatibility with polyvinyl chloride is poor. In an attempt to obtain epoxy stabilizers which are also primary solvent-type plasticisers, considerable industrial research effort has been expended in the preparation and evaluation of epoxidised esters of oleic acid, such as butyl epoxystearate and other alkyl epoxystearates, also obtainable from inexpensive fat sources such as tallow and grease. The compatibility of many of the monoalkyl epoxystearates is high, they impart good low temperature characteristics to polyvinyl chloride, and they are efficient plasticisers, as shown by their effect on modulus, elongation, and tensile strength. The lower monoalkylepoxystearates, however, frequently have poor

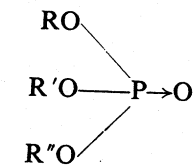
migration and volatility characteristics. When the molecular weight or chain length of the alkyl group of the ester moiety is increased sufficiently to reduce volatility loss to a satisfactory level, compatibility and efficiency are adversely affected.

During our work a large number of epoxy esters having quite variable structural characteristics have been prepared in an attempt to correlate the efficiency of epoxy esters as primary plasticisers with structure. It was reasoned that if both the acetyl and oxirane groups were present in the same molecule, efficient primary plasticisers having relatively low volatility and migration loss should be obtained. Therefore, special attention has been given to epoxidised diacetoglycerides from fats<sup>5</sup>. Information has recently been received, however, that light-induced hydrolysis may lead to undesirable acetic acid odours in their use<sup>6</sup>.

#### *Phosphorus Derivatives of Fats*

Groups containing the phosphorus atom are known to impart useful properties to plasticisers, and a number of phosphorus containing plasticisers are commercially available. None of these, however, contains the long-chain structures characteristic of fats. Recently a variety of long-chain phosphorus compounds has been prepared systematically.

As all of the commercially available phosphorus-containing plasticisers are phosphates, the first class of long-chain phosphorus compounds given attention was of trialkyl phosphates (Formula I)<sup>7</sup>. The primary objective was to determine whether symmetrical trialkyl phosphates with long alkyl chains were compatible with vinyl chloride-vinyl acetate copolymers (95-5). Tridodecyl phosphate was the trialkyl phosphate of shortest chain length prepared, because it was thought that any species of lower molecular weight would probably be too volatile. Tridodecyl phosphate, trioctadecyl phosphate, and trioctyl phosphate were incompatible; in fact, these compounds could not even be milled into the polymer at 300°F.

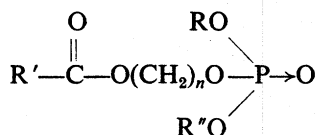


Alkyl phosphate  
Formula I

Since short-chain trialkyl phosphates (triethyl, tripropyl, and tributyl phosphates) are good solvent type plasticisers for the vinyl chloride-vinyl acetate copolymers, although admittedly much too volatile, it was thought that possibly one of these short alkyl chains could be replaced by a much longer aliphatic chain without loss in compatibility. A mixed trialkyl phosphate, diethyl dodecyl phosphate, was prepared and evaluated. This compound could easily be milled with the resin and yielded a very flexible sheet on moulding. The mechanical properties of the sheet were very good and a low Clash-Berg torsional modulus temperature was obtained ( $-53^{\circ}\text{C}$ ). Diethyl dodecyl phosphate, however, was too volatile, indicating that a longer alkyl chain should

be introduced to reduce the volatility still further. Diethyl octadecyl phosphate was then prepared and evaluated. Although it could be milled with the copolymer resin and yielded a flexible sheet, after 12 hours profuse migration occurred. On the other hand, diethyl oleyl phosphate milled easily and yielded a well plasticised sheet with good mechanical properties and low Clash-Berg temperature ( $-61^{\circ}\text{C}$ ). Apparently the interruption of the long aliphatic chain by a double bond provides a site for bonding with the resin so that the compound is compatible at the 35 per cent level, in contrast to the octadecyl compound.

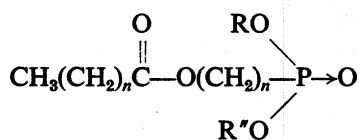
Since the mixed alkyl phosphates showed promise, efforts were next directed to the introduction of further compatibilising groups in the phosphorus containing fatty derivatives. A number of dialkyl acyloxy alkyl phosphates (Formula II) were prepared. While a number of the compounds investigated were unstable the dialkyl acyloxypropyl and acyloxybutyl phosphates (II,  $n = 3$  or  $4$ ) milled readily and were stable to milling conditions, they showed good compatibility, efficiency, and other mechanical properties, and they had exceptionally good low temperature characteristics. Five compounds were evaluated; their Clash-Berg temperatures ranged from  $-41^{\circ}$  to  $-67^{\circ}\text{C}$ . The latter value, the lowest the authors have observed for a plasticiser at the 35 per cent level, was obtained with diethyl oleo-oxypropyl phosphate.



Dialkylacyloxyalkyl phosphate

Formula II

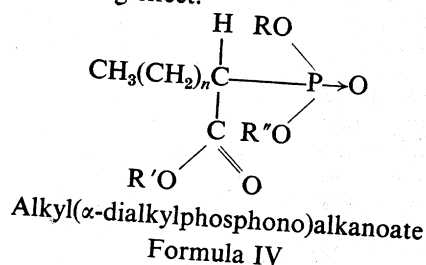
The next group of phosphorus derivatives explored was the phosphonates. They are known to be more stable to heat and hydrolysis than the analogous phosphates and little information was available in the literature on such compounds. The dialkylacyloxyphosphonates (Formula III) were the first group of this class to be examined. The dialkyl acyloxyalkylphosphonates milled well and showed good over-all properties comparable with those of closely related phosphates. The heat stability at  $160^{\circ}\text{C}$  of the milled and moulded sheets containing 35 per cent of phosphonates was far superior to that of sheets containing phosphates. However, the maximum length of the alkyl chain which yielded a compatible plasticiser was about  $\text{C}_{12}$ , a chain length similar to that observed previously.



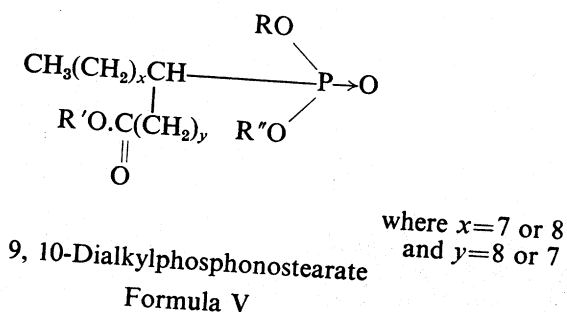
Dialkylacyloxyalkyl phosphonate

Formula III

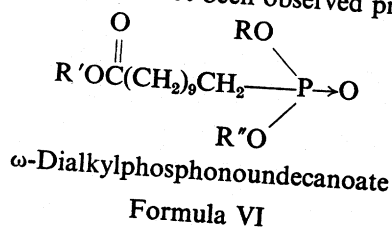
With the alkyl ( $\alpha$ -dialkylphosphono)alkanoates (Formula IV), this limitation on chain length apparently is not so rigorous since the ethyl ( $\alpha$ -diethylphosphono) stearate showed good over-all properties as a plasticiser. It may be concluded that the dialkylphosphono group in the  $\alpha$ -position of a fatty acid ester has an unusually high compatibilising effect.



All of the above long-chain phosphorus compounds in common with other efficient low temperature plasticisers show undesirably high migrations. However, this was not true with the 9, 10-dialkylphosphonostearates (Formula V), when a newly developed method of synthesis<sup>8</sup> made it possible to prepare and evaluate these compounds.



The 9, 10-dialkylphosphonostearates are outstanding in that they not only have a low and constant migration loss [8-9 per cent compared to 23 per cent for di(2-ethylhexyl)sebacate] but also impart good low temperature flexibility characteristics to polyvinyl chloride ( $-40^\circ$  to  $-50^\circ$ ). The  $\omega$ -dialkylphosphonoundecanoates (Formula VI) prepared by a similar method show somewhat higher migration losses, but even here two specific compounds have been found to be outstanding for the stiffness temperatures attainable. This desirable combination of characteristics has not been observed previously.



Comparison of the structures of these two groups of plasticisers shows a close similarity. The 9, 10-dialkylphosphonostearates, however, have an additional long branch on the carbon atom to which the dialkylphosphono group is attached whereas the phosphonoundecanoates have not. The lowest migration losses occur not only when the polar groups are widely separated but also when an additional branch is present in the molecule. In support of this conclusion, 9, 10-dialkylphosphonostearates have less than half of the migration losses of isomeric  $\alpha$ -dialkylphosphonostearates in which the polar groups are close together, and significantly lower migration losses than the  $\omega$ -dialkylphosphonoundecanoates in which the additional branch is absent. Whether the position of this branch with respect to a polar group is important cannot be decided until more compounds are available.

#### POLYMERS

The classical concept of fat polymerisation has involved reaction at the centres of unsaturation in the fatty acid chains. This concept would restrict application of the polymerisation reaction in fats and oils to those of the drying or semi-drying type. Little hope can be held for the use of animal fats in the field of polymerisation if one's thinking is limited to this particular type of reaction. Fortunately, however, several approaches do exist to the use of the saturated acids from animal fats in polymerisation reactions. One of the most obvious approaches is through the esterification of these saturated acids with unsaturated alcohols. This has been explored most thoroughly with the vinyl esters. Vinyl ester preparation by reaction of acetylene with fatty acids was first proposed by Reppe<sup>9</sup>. The esters can also be prepared by the acidolysis of vinyl acetate with the fatty acid. Both processes have been investigated to a considerable extent and a practical preference will depend upon a number of commercial variables<sup>10</sup>.

Probably the greatest potential for the use of vinyl stearate lies in its copolymerisation with other monomers to modify the physical properties, especially the flexing characteristics. Its use as an internal modifier or internal plasticiser offers numerous possibilities, but the products obtained differ in character from those obtained with external plasticisers, however. For example, they are characterised by less "life". Nevertheless numerous plastic items may be made which are internally modified, have outstanding impact-resistance characteristics, and no plasticiser loss by "bleeding" or extraction can possibly occur.

If one starts with the alcohols instead of the acids, vinylation with acetylene leads to the vinyl ethers. It was originally hoped that such products not containing the ester group would have improved stability. In general, this was not true and since the economics were less favourable, work on the ethers was not extended. Conversion of fats to alcohols does, however, permit the preparation of polymerisable derivatives of another sort, namely those in which the acid group carried the reactive segment of the molecule. Compounds of this sort are exemplified by the alkyl acrylates. Copolymerisation of these esters with vinylidene chloride has been studied extensively<sup>11</sup>.

Observations regarding the modifying characteristics of long chain vinyl esters coupled with the proved stabilising properties of epoxy compounds, suggested the investigation of vinyl epoxystearate and its copolymers. This

compound was prepared after considerable difficulty by the epoxidation of vinyl oleate<sup>12</sup>. However, careful consideration of the factors involved indicates that the technical advantages of using vinyl epoxystearate are probably outweighed by the economic disadvantages arising from difficulties in its preparation.

Finally it may be noted that the preparation of resinous polymers by curing epoxidised fatty materials with phthalic anhydride is now under examination<sup>13</sup>. In general, the resins are formed by heating the epoxide intermediate with phthalic anhydride in the presence of a catalytic amount of benzyltrimethylamine.

#### REFERENCES

1. Knight, H. B., Koos, R. E., Jordan, E. F. Jun., and Swern, D., *J. Amer. Oil Chemists' Soc.*, 1950, **27**, 281-284.
2. Knight, H. B., Witnauer, L. P., Palm, W. E., Koos, R. E., and Swern, D., *J. Amer. Oil Chemists' Soc.*, 1959, **36**, 382-388.
3. Swern, D., Billen, G., Findley, T. W., and Scanlan, J. T., *J. Amer. Chem. Soc.*, 1945, **67**, 1786-1789.
4. Swern, D., and Findley, T. W., U.S. Patent 2,569,502 (2.10.51).
5. Ault, W. C., and Feuge, R. O., U.S. Patent 2,895,966 (21.7.59).
6. Swern, D., and Knight, H. B., U.S. Patent 2,898,348 (4.8.60).
6. Informal private communications.
7. Swern, D., Palm, W. E., Ackerman, B., and Witnauer, L. P., *Chem. and Eng. Data Series*, 1958, **3**, 346-349.
8. Sasin, R., Olszewski, W. F., Russell, J. R., and Swern, D. J., *Amer. Chem. Soc.*, 1959, **81**, 6275-6277.
9. Reppe, W., German Patent 588,352 (1933), U.S. Patent 2,066,075 (1936).
10. Craig, L. E., Kleinschmidt, R. F., Miller, E. S., Wilkinson, J. M. Jun., Davis, R. W., Montross, C. F., and Port, W. S., *Ind. Eng. Chem.*, 1955, **47**, 1702-1706.
10. Redfield, C. S., Port, W. S., and Swern, D., *Ind. Eng. Chem.*, 1955, **47**, 1707-1710.
11. Jordan, E. F. Jun., Palm, W. E., Witnauer, L. P., and Port, W. S., *Ind. Eng. Chem.*, 1957, **49**, 1695-1698.
12. Silbert, L. S., Jacobs, Z. B., Palm, W. E., Witnauer, L. P., Port, W. S., and Swern, D., *J. Polymer Sci.*, 1956, **21**, 161-173.
13. Gelb, L. L., Ault, W. C., Palm, W. E., Witnauer, L. P., and Port, W. S., *J. Amer. Oil Chemists' Soc.*, 1959, **36**, 283-286.

[Received 11 April, 1960]

#### DISCUSSION

MR. K. J. HEDGEcock asked whether any work had been done using aryl as opposed to alkyl fatty phosphates as he thought that these might have better compatibility with vinyl resins.

DR. AULT replied that in general aryl phosphates had been used only for comparison purposes but there was some data available on triphenyl compounds although possibly insufficient work had been carried out on this aspect of the subject.

MR. C. DEVENNEY enquired about the compatibility of epoxidised soyabean oil having an oxirane content of about 7 per cent and whether epoxidised soyabean oil constituted the major part of the epoxy stabiliser field in the United States.

DR. AULT replied that the compatibility depended upon the identity of the other plasticisers present. Epoxidised soyabean oil was usually used in the United States at about 5 per cent. At higher figures difficulty might be caused without more knowledge about general formulation. The amount of epoxidised soya oil used per annum in the States was of the order of 30 million pounds and of all other fatty intermediates about one-third or one-fourth of that. It constituted the major part but by no means all of the epoxy stabiliser used.



September

W. C. AULT

MR. H. WARSON asked whether it was possible to epoxidise tung oil or eleaostearic acid and whether much work had been done with compounds of the type of vinyl epoxy stearates which should be able to form polymers through both the vinyl and epoxy groups. He also enquired whether it was possible to produce vinyl hydroxy or dihydroxy stearate by vinylolysis in view of the high reactivity of hydroxyl groups in this reaction.

DR. AULT replied that he was uncertain whether epoxidation of tung oil was possible, though with that type of unsaturation, epoxidation was usually more difficult and less complete. From a practical point of view he could not envisage epoxidised tung oil being used in the United States for economic reasons. Vinyl epoxy stearate had been made and polymerisation and co-polymerisation reactions studied to a considerable degree. It could be made by epoxidation of vinyl stearate but any proportion of oleate would impair the compatibility and it was difficult to synthesise without oleate. Some commercial interest had been shown in the compound but there had been as yet no manufacture on a commercial scale. He could not comment on the vinyl hydroxy stearates.

MR. D. FYSH enquired whether glycidyl epoxy stearate had been studied as a film former.

DR. AULT replied that although there had been some interest in this he did not know very much about it.

DR. A. S. FREEBORN asked whether the epoxy group in the epoxidised plasticisers served any function other than that of a stabiliser for taking up the hydrochloric acid produced on degradation of polyvinyl chloride.

DR. AULT replied that it was a very strong compatibilising group just as the ester or phosphate groups were strong polymerising groups.

DR. P. P. HOPF asked whether epoxidised trioleyl phosphate had been investigated as he would expect it to be more compatible than the more unsaturated esters. He also agreed that the epoxidised oils acted as more than hydrochloric acid acceptors for he had been unable to isolate a chlorhydrin.

DR. AULT had no comments on the epoxidation of trioleyl phosphate and agreed that the chlorhydrin had not been isolated.

MR. DEVENNEY asked whether epoxidised vegetable oils were used to any extent in alkyd resin formulation in the United States.

DR. AULT said that he had mentioned the reaction with phthalic anhydride which was related to alkyd resin formation but he had no knowledge of any direct uses in alkyd resins.

MR. I. C. R. BEWS enquired as to the possible carcinogenic or toxic effects of the epoxy compounds mentioned in the lecture.

DR. AULT replied that the general opinion in the States was that there would be less likelihood of undesirable effects than with many other single groupings which might find a use in plasticisers but he did not think that this was based on any real scientific or medical studies.

DR. HOPF added that there had been quite extensive work in the United Kingdom on this problem and that whilst there was definite reason to suspect terminal epoxy groups to be toxic, secondary epoxy groups were not so considered.

DR. AULT suggested that it was a question of the intermediates which might be formed and that in the case of epoxy stearic acid this should form dihydroxy stearic acid which was innocuous.

MR. A. G. ROBINSON asked whether any work had been carried out on the use of diethyl fatty phosphates in surface coatings, whether they were compatible with nitrocellulose to replace tricresyl phosphate and if there was any information as to durability or adhesion to substrates.

DR. AULT regretted that he had no information on this subject as although such studies were being carried out he had no report on them as yet.

MR. R. J. CARTER enquired as to the compatibility of the alkyl phosphates with polymethacrylates. He also commented that although Dr. Ault's primary interest was in the use of  $C_{18}$  chain lengths, could it not be anticipated that with polyvinyl chloride, a phosphate with three medium chain lengths, say eight carbon atoms each, would be more compatible than one with one  $C_{18}$  chain and two butyls?

DR. AULT replied that there was no information on polymethacrylate compatibility and that so far as mixed alkyl phosphates were concerned it might be possible to arrive at a satisfactory average for compatibility but no work of this nature had been carried out.

DR. R. ROWE asked for a comparison of the compatibility of epoxidised dimeric acid esters with linoleic acid esters.

DR. AULT replied that in general the epoxidised monomeric acid esters would be quite compatible whilst the epoxidised dimeric acid esters would be quite incompatible.

MR. N. R. FISK asked whether there was any information as to the availability in the United Kingdom of the compounds described in quantities suitable for experimental work even on a small scale.

DR. HOPF replied that most of them were available except the phosphonates.

DR. AULT added that the phosphonates were not available in America either, although he had heard that there were tentative arrangements being made to make them available for evaluation, in the near future.

DR. T. MALKIN proposed a vote of thanks to Dr. Ault and said that there could be no better use for inedible fats than as plasticisers and plastics. He thought that some consideration should be given to the precise function of a plasticiser and the relation of properties to the chemical identity of the groups on the chain and the lengths of chain between those groups.